



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: D21H 21/16, 17/16, 17/37, 17/45	A1	(11) International Publication Number: WO 97/05330 (43) International Publication Date: 13 February 1997 (13.02.97)
(21) International Application Number: PCT/US96/12231 (22) International Filing Date: 25 July 1996 (25.07.96) (30) Priority Data: 08/508,286 27 July 1995 (27.07.95) US (71) Applicant: CYTEC TECHNOLOGY CORP. [US/US]: Suite 1300, 1105 North Market Street, Wilmington, DE 19801 (US). (72) Inventor: WASSER, Richard, Barkman; 7 Dock Road, Norwalk, CT 06854 (US). (74) Agent: LAU, Bernard; Cytec Industries Inc., 1937 West Main Street, P.O. Box 60, Stamford, CT 06904-0060 (US).		(81) Designated States: AL, AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LS, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, TJ, TM, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: SYNTHETIC CATIONIC POLYMERS AS PROMOTERS FOR ASA SIZING**(57) Abstract**

Synthetic cationic polymers are used as promoters for alkenyl succinic anhydride sizing. The addition of certain synthetic cationic polymers that are reactive with alkenyl succinic anhydride are shown to improve the sizing efficiency of the hydrophobic, cellulose sizing material in papermaking. Synthetic cationic polymers were intended to replace starch as an effective promoter in papermaking.

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SYNTHETIC CATIONIC POLYMERS
AS PROMOTERS FOR ASA SIZING

Technical Field

5 This invention relates to emulsions using synthetic cationic polymers as promoters for alkenyl succinic anhydride sizing, and more specifically to an emulsion containing alkenyl succinic anhydride and a synthetic cationic polymer that enhances sizing efficiency and a method of using the same.

10 Background of the Invention

Sizing agents in the papermaking process are used to promote reduced water and ink absorption in the paper product as well as to resist aqueous acid and alkaline solutions. As used herein, the term "paper" is contemplated to include any sheet-like masses and molded products made from fibrous cellulosic materials which may be derived from both
15 natural and synthetic sources.

Paper is often sized with various materials to increase resistance to water as well as to other types of aqueous solutions. These materials are referred to as sizes or sizing and they may be introduced during the actual papermaking process. Alternatively, the sizes or sizing may be applied to the surface of the finished web or sheet.

20 One example of a sizing agent is alkenyl succinic anhydride ("ASA"). ASA, useful in the sizing of cellulose materials, has gained considerable commercial success in papermaking, particularly as an alternative to the conventional rosin-alum sizing system. The use of ASA as a sizing agent is well known in the art, as described in Farley and Wasser, "Sizing with Alkenyl Succinic Anhydride" In The Sizing of Paper, W.F. Reynolds,
25 Ed., TAPPI, 1989, Chapter 3. See also U.S. Patent No. 3,968,005, which is incorporated herein by reference.

ASA is water insoluble and hydrolytically unstable. Therefore, it must be emulsified at the paper mill prior to use. Specifically, the art requires that for retention the sizing agents be used in conjunction with a material that is cationic in nature, or is capable of
30 producing one or more cations or other positively charged groups. Emulsification is normally achieved by passing the ASA and a protective colloid, starch and/or synthetic polymer, through a device such as a homogenizer, high shear turbine pump, etc.

Cationic starch plays several important roles in ASA sizing. First, it aids in the generation of small particle size ASA emulsions. Small particle size, in the micron range,
35 is required for good sizing efficiency. Second, it imparts good physical stability to the

emulsion. ASA emulsions must be stable in order to prevent deposits and press picking once they have been added to the paper furnish. Third, it retains the emulsion on the fiber surfaces and promotes sizing efficiency. Sizing levels for a given amount of ASA are found to increase several-fold as the amount of cationic starch in the pulp furnish increases. Normally, cationic starch is used at a ratio of 2 to 4 times that of the ASA to give optimum sizing efficiency.

Certain problems arise with the use of cationic starch, however. For example, the starch must be cooked at the mill, thus requiring large scale cooking equipment and storage tanks. More importantly, starch is susceptible to biological degradation, resulting in slime growth and the creation of deposits on paper mill equipment, causing runnability problems in the form of press picking, felt filling and poor cylinder vat consistency control.

It may be desirable, in some cases, to make the ASA sizing system function independently of cationic starch. The variation in batch-to-batch starch viscosity and solids, and the need to cool the starch before emulsification can lead to unwanted variation in ASA emulsion particle size. Some paper mills do not like to use starch because of the difficult cooking and handling requirements. Others, where fine paper grades are made and where much of the ASA sizes are currently being used, require cationic starch for dry strength, but the mills would prefer to use lower cost cationic corn starches. Generally, more expensive cationic potato starch gives better results for ASA sizing.

Synthetic polymers as alternatives to cationic starch for ASA emulsification, and specifically to overcoming the problems associated with cationic starch, have been studied. The synthetic cationic polymers of the art as alternative to starch are not reactive with ASA. For example, U.S. Patent No. 4,657,946 teaches an improved emulsification of ASA sizing agent by using cationically charged water soluble vinyl addition polymers. The '946 patent teaches a paper sizing method and emulsion using cationically charged, water soluble, vinyl addition polymers and condensation polymers that provide improved emulsification of alkenyl succinic anhydride sizing agents. U.S. Patent No. 5,224,993 teaches a saponified sizing agent for paper derived from the dehydration condensation of an alkenyl succinic anhydride and an organic carboxylic acid with a polyalkylene polyamine and the saponification of the remaining carboxyl groups with alkali following the dehydration condensation. U.S. Patent No. 4,629,655 teaches a size composition as a solid product produced by mixing a cationic polymer suitable for functioning as a size retention aid and a size suitable for sizing a substrate. The process for sizing a substrate in the '655 patent comprises dispersing the solid in an aqueous mixture, applying the resultant mixture to a substrate, and causing the size to be fixed to the substrate thereby. However, the synthetic

cationic polymers of the art have only been marginally successful as a suitable replacement for starch. None of these synthetic cationic polymers contain functional groups that are reactive with ASA. The synthetic cationic polymers of the art which serve as additives and co-emulsifying agents for ASA sizing do not enhance sizing (or do not serve as good promoters).

Various patents disclosing polymers that are reactive with ASA do not teach the use for promoting the efficiency of sizing agent. For example, these patents include U.S. Patent No. 5,232,553, which teaches a papermaking process using polyvinylaminals in which the paper product obtained from the pulp slurry contains fine particles of material. The '553 patent relates to the use of poly(vinylamine) and aldehyde for increasing the retention of the fines in the paper product.

In developing an alternative to starch in the ASA emulsions, it is generally found that producing a synthetic cationic polymer having high viscosity to generate small particles size emulsions and acting as a retention aid is not particularly difficult. The difficulty lies in developing a synthetic cationic polymer that promotes the sizing efficiency of ASA by providing ASA reactive groups that can anchor the ASA to the fiber surface.

Various other patents make use of similar synthetic cationic polymers but do not teach an increase in sizing efficiency in papermaking. U.S. Patent No. 4,217,214 teaches the use of high molecular weight polyvinylamine hydrochloride for the flocculation of suspended solids in water purification or waste water clarification systems. U.S. Patent No. 4,957,977 teaches a flocculating agent and paper strength increasing agent using a vinylamine copolymer and a process for producing the vinylamine polymer. U.K. Patent Application GB 2,268,758A teaches a paper wet strength improvement by wet- or dry-end addition of an amine-functional poly(vinyl alcohol) and a cellulose reactive size which is a 4 or 5 membered cyclic ester or anhydride having one or more alkyl or alkenyl substituents of 4 or more carbon atoms and having a total of at least 8 carbon atoms in the substituents. In fact, patents that are directed to synthetic cationic polymers in the art do not specifically relate to increasing the efficiency of paper sizing.

While the synthetic agents of the art have met with some success, there has been a need in the paper industry to produce a more effective cationic agent that is useful as a promoter for sizing to avoid the problems generally associated with cationic starch. Such a cationic agent would be reactive with ASA and would significantly enhance sizing efficiency.

Summary of the Invention

According to the present invention, there is provided methods in papermaking for improving the sizing efficiency of a hydrophobic, cellulose sizing material which comprises adding thereto a synthetic cationic polymer that is reactive with said sizing material. Groups that are reactive with ASA include primary amine and hydroxyl. The preferred sizing material is alkenyl succinic anhydride. The preferred synthetic cationic polymer comprises a copolymer of primary amine. Also provided is a synthetic cationic polymer which contains one or more non-sizing reactive monomers, particularly, non-ASA reactive monomers, like acrylic acid. For the purpose of this invention, the term non-sizing reactive monomer (or non-ASA reactive monomer) refers to a monomer that does not result in a significant reaction with a sizing material. The synthetic cationic polymer may be a copolymer of vinyl alcohol and vinylamine. The synthetic cationic polymer may also be a copolymer of acrylamide and vinylamine.

There is also provided a method in papermaking for improving the sizing efficiency of a hydrophobic, cellulose sizing material which comprises adding to a cellulose sizing agent an effective amount of a synthetic cationic polymer containing hydroxyl and/or primary amine groups. Preferably the polymer comprises about 50 to about 99 mole % vinylalcohol and about 50 to about 1 mole % vinylamine.

There is provided a method in papermaking for improving the sizing efficiency of an alkenyl succinic anhydride comprising adding thereto a synthetic cationic polymer of about 20 to about 90 mole % acrylamide and about 80 to about 10 mole % vinylamine.

This invention discloses an alkaline sizing emulsion for improving the sizing efficiency in papermaking comprising a hydrophobic cellulose sizing material and a copolymer of cationic vinylamine that is reactive with said sizing material. Preferably, the sizing material is alkenyl succinic anhydride. It is preferable to have as a copolymer comprising a synthetic polymer of about 20 to about 90 mole % acrylamide and about 80 to about 10 mole % vinylamine. It is also preferable to have as a copolymer comprising a synthetic polymer of about 50 to about 99 mole % vinylalcohol and about 50 to about 1 mole % vinylamine.

There is also provided an alkaline sizing emulsion comprising an alkenyl succinic anhydride sizing material and an effective amount of a synthetic cationic polymer reactive with the sizing material wherein the polymer contains hydroxyl and/or primary amine groups.

As provided herein, the term "effective amount" is defined as the quantity of material needed to increase the sizing efficiency of a sizing agent.

Detailed Description of the Preferred Embodiments

Various synthetic cationic polymers were evaluated as replacements for cationic starch that is normally used in the ASA paper sizing process. Cationic starch has been shown to be a good sizing promoter for ASA.

To demonstrate the effect of various synthetic cationic polymers on ASA sizing, promotion performance based on an increase in sizing efficiency using cationic starch were evaluated in comparison with a variety of different synthetic cationic polymers. It should be noted that starch is distinct from the synthetic cationic polymers because starch is a natural substance, rather than synthetic.

Paper handsheets containing the size and promoter were prepared and used for sizing evaluation. For the purpose of this invention, a handsheet is comprised of pulp, fillers, sizing agent (ASA) and promoter (a cationic starch or a synthetic cationic polymer).

Emulsification of ASA using cationic polyacrylamide:

For each handsheet evaluation, an ASA emulsion is prepared in deionized water. The emulsification procedure proceeds as follows: 24.0 g of deionized water was weighed into a small (about 35 mL capacity) stainless steel blender jar. About 1 g of ASA (weighed by difference) is added and the blender is run at high speed for five minutes. Based on the calculated ASA concentration, the sample was immediately diluted to 0.25% with cold, pH 3 deionized water to minimize hydrolysis. The sample was kept on ice until used for the handsheet evaluation. Particle size was estimated to be in the 1.5 to 2 micron range.

A variety of synthetic cationic polymers containing copolymers of amide and amine groups, as well as alcohol and amine groups are within the scope of the invention. Each of the polymers and copolymers was selected for evaluation because each contains functional groups (i.e., primary amine or hydroxyl) that can react with ASA.

Cationic polyvinylalcohol may contain 6 mole % vinylamine groups (PVOH/PVA) and have a molecular weight in the range of from 80 to 140 k daltons. The copolymer was prepared by hydrolysis of a copolymer of vinylacetate and N-vinyl formamide.

Polyvinylamine (PVA) and polyvinylamine.HCl (PVA/HCl) are contemplated as useful in this invention. The PVA is of a low molecular weight and is supplied as a 12.8% solution. The PVA.HCl may be a medium molecular weight powder.

Polyallylamine.HCl (PAA) and copolymer of allylamine and diallylamine.HCl (PAA/PDAA) are also contemplated as being useful in this invention. The PAA has an average molecular weight of about 100 k daltons and is supplied as a 40% aqueous solution. The PAA/PDAA has a weight average molecular weight of 50 k daltons.

The Hofmann degradation of polyacrylamide using sodium hypochlorite introduces primary amine and carboxyl groups. Samples were prepared containing about 40 mole % primary amine using polyacrylamide samples of four different molecular weights ranging from 14 to 200 k daltons using the procedure from Tanaka (see, H. Tanaka, J. Polymer Science: Polymer Letters Edition 16, 87-89 (1978)).

Table I presents the Hofmann degradation products of polyacrylamide. In analyzing the amine and carboxyl contents of the Hofmann degradation products, it is shown that the variation in molecular weights does not significantly change the concentration of amine content, carboxyl content or isoelectric pH.

Table I

<u>Example</u>	<u>Molecular weight</u> (k daltons)	<u>mole % amine</u>	<u>mole % carboxyl</u>	<u>Isoelectric pH</u>
1	200	40	14	9
2	77	47	24	9
3	47	60	24	8
4	14	47	14	8.5

In addition to ASA-reactive synthetic cationic polymers, various non ASA- reactive synthetic cationic polymers were considered as promoters, for example, acrylamide/methacryloxyethyltrimethyl ammonium chloride (acrylamide/Q6) copolymer, polyethylenimine (polymer with average molecular weight of 50 to 60 k daltons, containing mostly secondary amine groups), Mannich quaternary of polyacrylamide, and terpolymers of acrylamide, acryloxyethyltrimethylammonium chloride (Q9) and alkyl methacrylate.

The ASA primarily used is ACCOSIZE® 18 (available from Cytec Industries Inc.).

Promotion of ASA sizing:

The sizing level achievable with ASA significantly increases (is promoted) as the amount of cationic starch in the system increases. The magnitude of the increase and that sizing continues to increase even with relatively large amount of cationic starch, up to 3:1 ratio of starch to ASA. Because of this effect, a high ratio of cationic starch to ASA is used in current commercial practice. It does not matter whether the cationic starch is part of the ASA emulsion or whether it is added separately to the furnish. As shown in this invention, the sizing level of an ASA sizing agent may also be significantly increased by increasing the concentration of synthetic cationic polymers that are reactive with ASA.

Handsheet evaluation of polymers as ASA promoters

The handsheet experiments are done using the following procedure. The furnish is a 50/50 mixture of bleached hardwood and softwood kraft pulps beaten to a Canadian Standard Freeness of 500 to which 15% by weight of precipitated calcium carbonate is added and the pH adjusted to 7.5. While stirring, a batch of 0.6% consistency stock containing 10g of fiber is treated with the promoter, followed by a given dosage of ASA emulsion, then with 1.0 lb/ton of anionic polyacrylamide retention aid. Fifteen seconds of contact time is allowed between each addition. Three-2.8 g handsheets (50 lb/Tappi ream) are formed, pressed with 1-1/2 weights, and dried one minute on the rotary drum drier at 240°F.

Basis weight and sizing are measured on the sheets after conditioning for at least 24 hours at 23 °C and 50% R.H. The handsheets are tested for ink penetration using a sizing test of the type described in Tappi Standard T-530 pm-83. It measures the elapsed time after contacting one side of the paper with ink for the reflectance of the opposite side to fall to 80% of its initial value. The ink is the same as described in T-530 pm-83, but contains no formic acid and is buffered to pH 7. The tests are normalized to 50 lb/Tappi ream basis weight assuming sizing is proportional to the cube of the basis weight.

While it is apparent that the invention herein disclosed is well calculated to describe the invention stated above, it should well be appreciated that numerous modifications and embodiments may be devised by those skilled in the art, and it is intended that the appended claims cover all such modifications and embodiments as fall within the true spirit and scope of the present invention.

EXAMPLES 5 TO 14 (Comparative)

Example 5 of Table II shows the results of an evaluation of the ink penetration of an ASA emulsion made with a 90/10 mole ratio AMD/Q6 copolymer. This same emulsion was then post-diluted with either additional AMD/Q6 copolymer (a synthetic cationic polymer) or with cationic starch. The ASA dosage was 0.15% on fiber in all the examples. Post-dilution with additional AMD/Q6 copolymer (Examples 6 to 9) shows that the sizing efficiency does not increase appreciably, since the copolymer is not reactive with ASA. Examples 10 to 14 show that the AMD/Q6 copolymer post-diluted with cationic starch provided marked increase in sizing efficiency. As used herein, ink penetration is provided for in seconds. It is shown that the effect of the increase in sizing efficiency is attributed to the cationic starch (which is ASA-reactive) and not to the AMD/Q6 copolymer (which is not ASA-reactive).

Table II

	<u>Example</u>	<u>Post Dilution with Cationic Polymer (Ratio to ASA)</u>	<u>Post Dilution with Cationic Starch (Ratio to ASA)</u>	<u>Ink Penetration (sec)</u>
5	5 (Initial emulsion)	0.13	-	70
	6	0.5	-	138
	7	1.0	-	117
	8	2.0	-	64
10	9	3.0	-	86
	10	-	0.5	187
	11	-	1.0	254
	12	-	2.0	329
	13	-	3.0	349
15	14	-	4.0	396

EXAMPLES 15 TO 23 (Comparative)

Table III presents results of an evaluation that is similar to that presented in Table II. The 90/10 mole ratio AMD/Q6 copolymer of these examples is made by inverse emulsion techniques. Example 15 shows the sizing obtained with ASA emulsion made using the AMD/Q6 copolymer. The ASA dosage is 0.15% on fiber in all the examples. This same emulsion is then post diluted with either additional AMD/Q6 copolymer (Examples 16 to 18) or with cationic starch (Examples 19 to 23). These examples (Examples 15 to 18) show that the addition of inverse emulsion AMD/Q6 copolymer does not increase sizing efficiency since the copolymer is not reactive with ASA. Examples 19 to 23 show that the inverse AMD/Q6 copolymer diluted with cationic starch provided marked increase in sizing efficiency. It is shown that the effect of the increase in sizing efficiency is attributed to the cationic starch (which is ASA-reactive) and not to the AMD/Q6 copolymer (which is not ASA-reactive).

Table III

	<u>Example</u>	<u>Post Dilution with Cationic Polymer (Ratio to ASA)</u>	<u>Post Dilution with Cationic Starch (Ratio to ASA)</u>	<u>Ink Penetration (sec)</u>
35	15 (Initial emulsion)	0.13	-	62
	16	0.5	-	78
	17	1.0	-	35
	18	2.0	-	11
40	19	-	0.5	130
	20	-	1.0	189
	21	-	2.0	257
	22	-	3.0	290
	23	-	4.0	340

EXAMPLES 24 TO 32 (Comparative)

Table IV shows the results of an evaluation that is similar to those presented in Tables II and III. In this case, the synthetic cationic copolymer is 99/1 mole ratio AMD/Q9. An ASA emulsion is prepared using water only, Example 24. The ASA dosage was 0.125% on fiber in all of the examples. This same emulsion is then post diluted with either AMD/Q9 copolymer (Examples 25 to 27) or with cationic starch (Examples 28 to 32). These examples demonstrate that the addition of AMD/Q9 copolymer does not increase sizing efficiency since the copolymer is not reactive with ASA. Post dilution with cationic starch provides a marked increase in sizing efficiency. It is shown that the effect of the increase in sizing efficiency is attributed to the cationic starch (which is ASA-reactive) and not to the AMD/Q9 copolymer (which is not ASA-reactive).

Table IV

Example	Post Dilution with Cationic Polymer (Ratio to ASA)	Post Dilution with Cationic Starch (Ratio to ASA)	Ink Penetration (sec)
24 (initial emulsion)	-	-	6
25	0.5	-	8
26	1.0	-	4
27	2.0	-	5
28	-	0.35	40
29	-	0.6	77
30	-	1.2	89
31	-	2.4	157
32	-	4.8	179

EXAMPLES 33 TO 41 (Comparative)

Table V shows that the results of an evaluation of sizing as a function of promoter dosage for various promoters. Each of the examples in Table V is conducted using 0.2% on fiber of ASA. Examples 33 to 35 use a 18/20/2 mole percent terpolymer of acrylamide/Q9/n-dodecylmethacrylate terpolymer. This is a non-ASA reactive polymer. Examples 36 to 38 use cationic potato starch as the promoter. Examples 39 to 41 use PVOH/PVA as the promoter. Ink penetration is provided for in seconds. These examples show that the promotion effect of PVOH/PVA, an ASA-reactive polymer, increases the sizing efficiency by increase in dosage.

Table V

<u>Example</u>	<u>Dosage of Cationic Polymer (% on fiber)</u>	<u>Ink Penetration (sec)</u>
5		
33	0.05	2
34	0.10	2
35	0.20	2
10		
36	0.05	10
37	0.10	5
38	0.20	58
15		
39	0.05	44
40	0.10	48
41	0.20	195

EXAMPLES 42 TO 49 (Comparative)

Table VI presents the results of an evaluation of the sizing as a function of promoter dosage for various promoters. Each of the examples in Table VI are conducted using 0.15% on fiber. Examples 42 to 45 use cationic potato starch as the promoter. Examples 46 to 49 use PVOH/PVA as the promoter. Other parameters of this analysis are similar to those of Table V (Examples 33 to 41). Table VI demonstrates that PVOH/PVA is a more effective promoter than cationic potato starch (over the range of 0.075 to 0.45 lb/ton). These examples show that the promoter efficiency is a function of promoter concentration. Here, the PVOH/PVA is a much more effective promoter than cationic potato starch when the cationic polymer (either the synthetic cationic polymer or the starch) concentration is less than about 0.45% on fiber.

Table VI

<u>Example</u>	<u>Dosage of Cationic Polymer (% on Fiber)</u>	<u>Ink Penetration (sec)</u>
35		
42	0.075	160
43	0.15	157
44	0.30	194
45	0.45	222
40		
46	0.075	251
47	0.15	269
48	0.30	315
49	0.45	214

EXAMPLES 50 TO 55 (Comparative)

Table VII presents the results of an evaluation of sizing as a function of promoter dosage for various promoters, as in Table V (Examples 33 to 41). The emulsions of Table VII are prepared in the presence of either the PVOH/PVA or the cationic potato starch at 0.5/1 ratio to ASA. After emulsification, additional PVOH/PVA or cationic potato starch is added to the furnish to give dosages of 0.075, 0.15 or 0.3% on fiber. Examples 50 to 52 use cationic potato starch as the promoter. Examples 53 to 55 use PVOH/PVA, an ASA-reactive polymer, as the promoter. These examples demonstrate that the promoter efficiency is a function of the sizing concentration and the reactivity of the promoter with the sizing material.

Table VII

<u>Example</u>	<u>Dosage of Cationic Polymer (% on Fiber)</u>	<u>Ink Penetration (sec)</u>
50	0.075	140
51	0.15	232
52	0.30	171
53	0.075	208
54	0.15	254
55	0.30	314

EXAMPLES 56 TO 70 (Comparative)

Table VIII shows the results of an evaluation of sizing as a function of promoter dosage for various promoters, as in Table VI (Examples 42 to 49). Examples 56 to 59 use polyethylenimine as the promoter. Example 60 to 63 use a Hofmann degradation product as the promoter (Table I, Example 1). Examples 64 to 66 use cationic potato starch as the promoter. Examples 67 to 70 use PVOH/PVA as the promoter. These examples show that ASA-reactive synthetic cationic polymers (both PVOH/PVA and the Hofmann degradation product) provide promoting effect to ASA sizing. The polyethylenimine, which is not ASA-reactive, does not.

Table VIII

<u>Example</u>	<u>Dosage of Cationic Polymer (% on fiber)</u>	<u>Ink Penetration (sec)</u>
5		
56	0.075	2
57	0.15	4
58	0.30	2
59	0.45	2
10		
60	0.075	28
61	0.15	92
62	0.30	242
63	0.45	184
15		
64	0.075	111
65	0.15	144
66	0.45	282
20		
67	0.075	225
68	0.15	285
69	0.30	434
70	0.45	350

25 **EXAMPLES 71 TO 82 (Comparative)**

Table IX shows the results of an evaluation of sizing as a function of promoter dosage for various promoters, as in Table VI (Examples 42 to 49). The dosage of ASA is 0.2% on dry fiber. Examples 71 to 73 use a Mannich quaternary of polyacrylamide as the promoter. Examples 74 to 76 use cationic potato starch as the promoter. Examples 77 to 79 use PVOH/PVA as the promoter. Examples 80 to 82 use a Hofmann degradation product as the promoter (Table I, Example 1). This experiment shows that the two ASA-reactive synthetic cationic polymers (PVOH/PVA and the Hofmann degradation product) provide promoting effect to sizing. The Mannich quaternary of polyacrylamide, which is not ASA-reactive, does not.

Table IX

	<u>Example</u>	<u>Dosage of Cationic Polymer (% on fiber)</u>	<u>Ink Penetration (sec)</u>
5	71	0.075	2
	72	0.15	2
	73	0.30	2
10	74	0.15	7
	75	0.30	24
	76	0.45	101
15	77	0.0375	40
	78	0.075	45
	79	0.15	129
20	80	0.075	73
	81	0.15	72
	82	0.30	177

25 EXAMPLES 83 TO 106 (Comparative)

Table X shows the results of an evaluation of sizing as a function of promoter dosage for various promoters, as in Table VI (Examples 42 to 49). 0.15% ASA on fiber is used. Examples 83 to 85 use PAA/PDAA of 50 k daltons molecular weight as the promoter. Examples 86 to 88 use PAA of 100 k daltons molecular weight as the promoter. Examples 89 to 91 use a Hofmann degradation product of 14 k daltons molecular weight (Table 1, Example 4) as the promoter. Examples 92 to 94 use a Hofmann degradation product of 47 k daltons molecular weight (Table 1, Example 3) as the promoter. Examples 95 to 97 use a Hofmann degradation product of 77 k daltons molecular weight (Table 1, Example 2) as the promoter. Examples 98 to 100 use a Hofmann degradation product of 200 k daltons molecular weight (Table 1, Example 1) as the promoter. Examples 101 to 103 use cationic potato starch as the promoter. Examples 104 to 106 use PVOH/PVA as the promoter. These examples show that the promoting effect of the Hofmann degradation products increases with increasing molecular weight. Also, these examples show that the promoting effect of the Hofmann degradation products increases with increasing amount of the promoter with the sizing material.

Table X

	<u>Example</u>	<u>Dosage of Cationic Polymer (% on fiber)</u>	<u>Ink Penetration (sec)</u>
5	83	0.075	11
	84	0.15	40
	85	0.30	29
10	86	0.075	2
	87	0.15	1
	88	0.30	3
	89	0.075	2
15	90	0.15	1
	91	0.30	7
	92	0.075	2
	93	0.15	2
20	94	0.30	2
	95	0.075	15
	96	0.15	20
	97	0.30	111
25	98	0.075	71
	99	0.15	194
	100	0.30	236
30	101	0.15	236
	102	0.30	312
	103	0.45	373
	104	0.075	308
35	105	0.15	491
	106	0.30	389

40 EXAMPLES 107 TO 130 (Comparative)

Table XI shows the comparative results of an evaluation of the ink penetration as a function of promoter dosage for various promoters, as in Table X (Examples 83 to 106). Examples 107 to 109 use a Hofmann degradation product of 14 k daltons molecular weight (Table I, Example 4) and Examples 110 to 112 use a Hofmann degradation product of 47 k daltons molecular weight (Table I, Example 3) as the promoter. Examples 113 to 115 use a Hofmann degradation product of 77 k daltons (Table I, Example 2) as the promoter. Examples 116 to 118 use a Hofmann degradation product of 200 k daltons molecular

weight (Table 1, Example 1) as the promoter. Examples 119 to 121 use PVA as the promoter. Examples 122 to 124 use PVA.HCl as the promoter. Examples 125 to 127 use PVOH/PVA as the promoter. Examples 128 to 130 use cationic potato starch as the promoter. These examples show that both PVA and PVA.HCl are effective promoters for ASA. Both are ASA-reactive. It again shows that PVOH/PVA is an effective promoter, and that the effectiveness of the Hofmann degradation products increase with increasing molecular weight.

Table XI

10	<u>Example</u>	<u>Dosage of Cationic Polymer (% on fiber)</u>	<u>Ink Penetration (sec)</u>
15	107	0.30	4
	108	0.45	5
	109	0.60	60
20	110	0.30	1
	111	0.45	1
	112	0.60	1
25	113	0.15	6
	114	0.30	24
	115	0.45	127
30	116	0.075	194
	117	0.15	153
	118	0.225	240
35	119	0.15	258
	120	0.30	449
	121	0.45	260
40	122	0.15	129
	123	0.30	477
	124	0.45	406
45	125	0.0375	178
	126	0.075	280
	127	0.15	337
50	128	0.15	108
	129	0.30	334
	130	0.45	326

EXAMPLES 131 TO 154 (Comparative)

Table XII presents a further comparative evaluation of PVOH/PVA polymer as a sizing promoter for ASA. The performance of PVOH/PVA polymer as sizing promoter is compared to the use of cationic starch as the promoter. The synthetic polymer is evaluated under varying mole percent of PVA in the PVA/PVOH polymer as well as under varying molecular weight and dosage of the PVA/PVOH polymer. Each evaluation is conducted using 0.15 mole % on fiber of ASA. It is shown that at higher PVA mole % content (i.e., at 6 or 18 mole %), the PVOH/PVA promoter is more efficient than cationic starch. At levels of 3 mole % of PVA or less, the copolymer is not effective as a promoter. It is also shown that better efficiency is obtained with higher molecular weight samples.

Table XII

	<u>Example</u>	<u>PVA</u> mole %	<u>Cationic</u> <u>Starch</u> (% on fiber)	<u>Molecular</u> <u>Weight</u> (k daltons)	<u>Dosage</u> (% on fiber)	<u>Ink</u> <u>Penetration</u> (sec)
15	131	<1	--	50-120	0.15	1
	132	<1	--	50-120	0.30	1
	133	<1	--	50-120	0.45	1
20	134	3	--	50-120	0.15	1
	135	3	--	50-120	0.30	1
	136	3	--	50-120	0.45	1
25	137	6	--	36	0.0375	5.5
	138	6	--	36	0.075	21
	139	6	--	36	0.15	48
30	140	6	--	95	0.0375	1
	141	6	--	95	0.075	23
	142	6	--	95	0.15	98
	143	6	--	80-140	0.0375	47
	144	6	--	80-140	0.075	119
35	145	6	--	80-140	0.15	378
	146	18	--	75	0.0375	30
	147	18	--	75	0.075	259
	148	18	--	75	0.15	204
40	149	--	0.15	--	--	34
	150	--	0.15	--	--	13.6
	151	--	0.30	--	--	239
	152	--	0.30	--	--	271
45	153	--	0.45	--	--	275
	154	--	0.45	--	--	540

EXAMPLES 155 TO 159 (Comparative)

The paper that is used for the examples in Table XIII is made on a pilot paper machine. The ASA is emulsified either with a copolymer of acrylamide/methyl chloride quaternary salt of dimethylaminoethyl methacrylate (AMD/Q6) or with cationic potato starch.

5 The emulsion is added to the pulp at the down leg of the stuff box. ASA dosage is kept constant at 0.175%. The furnish is 70/30 bleached hardwood/softwood with 25% (on dry fiber) added precipitated CaCO_3 . In Example 155, the AMD/Q6 copolymer is provided in a final ratio to ASA of 0.13/1. In Example 156, the total AMD/Q6 copolymer is provided as in Example 155, but with additional polymer addition bringing the final ratio of AMD/Q6 to

10 ASA as 1.0/1. In Example 157, the ASA emulsion is made using a 90/10 AMD/Q6 inverse emulsion copolymer, with a final polymer/ASA ratio of 0.13/1. The result of these three examples show the average sizing for Examples 155, 156 and 157 as 20, 41 and 5 seconds, respectively. This demonstrates that the sizing was low, relative to the standard emulsions. Increasing the level of copolymer from 0.13:1 to 1:1 resulted only in a small

15 increase in sizing. It is shown that synthetic cationic polymers do not give sizing (or increase sizing efficiency) if the polymer is not reactive with the sizing material. In comparison, Examples 158 and 159 are ASA emulsions made using cationic starch in a ratio to ASA of 2.1/1. The much higher sizing values show the promoting effect of the ASA reactive cationic starch.

Table XIII

<u>Example</u>	<u>Ratio of Cationic Starch</u>	<u>Ratio of Cationic Polymer</u>	<u>Ink Penetration (sec)</u>
155	-	0.13	20
156	-	1.0	41
157	-	0.13	5
158	2.1	-	225
159	2.1	-	219

WHAT IS CLAIMED IS:

1. A method in papermaking for improving the sizing efficiency of alkenylsuccinic anhydride which comprises adding thereto a synthetic cationic polymer that is reactive with said anhydride

5 2. The method of claim 1 wherein said cationic polymer comprises a copolymer of a primary amine.

3. The method of claim 1 wherein said cationic polymer is a copolymer of about 50 to about 99 mole % vinylalcohol and about 50 to about 1 mole % vinylamine.

10 4. The method of claim 1 wherein said cationic polymer is a copolymer of about 20 to about 90 mole % acrylamide and about 80 to about 10 mole % vinylamine.

5. A method in papermaking for improving the sizing efficiency of a hydrophobic, cellulose sizing material which comprises adding to a cellulose sizing agent an effective amount of a synthetic cationic polymer containing hydroxyl or primary amine groups.

15 6. A method in papermaking for improving the sizing efficiency of an alkenylsuccinic anhydride which comprises adding thereto a synthetic cationic polymer comprising about 50 to about 99 mole % vinylalcohol and about 50 to about 1 mole % vinylamine.

20 7. A method in papermaking for improving the sizing efficiency of an alkenylsuccinic anhydride which comprises adding thereto a synthetic cationic polymer of about 20 to about 90 mole % acrylamide and about 80 to about 10 mole % vinylamine.

8. An alkaline sizing emulsion for improving the sizing efficiency in paper making comprising

A. alkenylsuccinic anhydride; and

25 B. a copolymer of cationic vinylamine that is reactive with said sizing material.

9. An alkaline sizing emulsion of claim 8 wherein said synthetic polymer comprises a copolymer of about 20 to about 90 mole % acrylamide and about 80 to about 10 mole % vinylamine.

30 10. An alkaline sizing emulsion of claim 8 wherein said synthetic polymer comprises a copolymer of about 50 to about 99 mole % vinylalcohol and about 50 to about 10 mole % vinylamine.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21H21/16 D21H17/16 D21H17/37 D21H17/45

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	GB 2 268 758 A (AIR PROD & CHEM) 19 January 1994 cited in the application ---	
A	US 4 657 946 A (RENDE DOMINIC S ET AL) 14 April 1987 cited in the application ---	
A	EP 0 200 504 A (ALLIED COLLOIDS LTD) 5 November 1986 -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

12 November 1996

Date of mailing of the international search report

- 4. 12. 96

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